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博 士 学 位 论 文

碳纳米管负载/促进合成气制低碳混合醇 Ni-Mo-K 氧化物基催化剂的研究

Study of MWCNTs Supported/Promoted Ni-Mo-K Oxide-Based Catalysts for Higher Alcohol Synthesis from Syngas

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扩展式中文摘要

煤基低碳醇醚燃料（包括甲醇、低碳混合醇和二甲醚）是基于能源化工原料多样化具有战略意义的燃料化学品。甲醇和低碳醇均已被证实是高辛烷值、低污染的车用合成燃料或燃料添加剂。自上个世纪 70 年代末世界经济受二次石油危机冲击后，由煤（或天然气）基合成气制取低碳混合醇的研究一度受到重视并取得一定进展；但迄今的低碳醇合成工艺，其原料合成气单程转化率及生成 C_{2+}-醇的选择性均较低，大多数体系的主要产物仍是甲醇或低碳烃，而非低碳（C_{2+}）醇，至今国际上尚无大型化低碳醇合成生产装置。近年来由于环保方面的原因，甲基叔丁基醚（MTBE）作为油品添加剂在一些国家和地区已被禁用，使得低碳醇作为油品添加剂的实用价值倍增，低碳醇合成工艺的工业化重新引起燃料化工界的兴趣。如何提高催化剂的活性和选择性以提高生产过程的效率，成为制约低碳醇合成工艺实用化和工业化的技术瓶颈。

多壁碳纳米管（简写为 CNTs）自 1991 年发现以来，人们对它的兴趣与日俱增。这类新型纳米碳材料在结构上与中空的石墨纤维相近，但其结构规整性较高，具有石墨化的管壁、纳米级的管腔、由 sp^2-C 构成的表面，并展现出良好的导电导热性、以及对 H_2 的吸附活化并促进吸附氢溢流的优良性能，所有这些使 CNTs 很有希望成为新型的催化剂载体或促进剂。迄今报道有关 CNTs 的催化应用领域涵盖选择加氢、氢甲酰化、氨合成、F-T 合成、甲醇/低碳醇合成、脱氢、选择氧化和电催化等。从化学催化角度考虑，碳纳米管对 H_2 强的吸附活化能力以及对氢溢流的促进作用很值得注意；利用某些过渡金属对 CNTs 进行适当修饰可望进一步提高其助催化性能。

本文开展 CO 加氢制低碳醇用的 CNTs 促进的高效新型 Ni-Mo-K 氧化物基催化剂的开发研究，从负载型 Ni-Mo-K 催化剂的应用基础研究入手，在初步弄清 CNTs 促进作用的基础上，进而研发出一类金属 Ni 修饰 CNTs 促进的高效新型 Ni-Mo-K 氧化物基催化剂，取得如下兼具理论和实用价值的重要进展。

1. CO 加氢制低碳醇用 CNTs 负载 Ni-Mo-K 氧化物基催化剂的开发研究

1.1 CNTs 负载 Ni-Mo-K 氧化物基催化剂的制备及催化性能

用自行制备的一种鱼骨型多壁碳纳米管（记为 CNTs）作为载体，由分步等容浸渍法制备 CNTs-负载的 Ni-Mo-K 氧化物基催化剂（记为 $x\%Ni_iMo_jK_k$/CNTs，x%为质量分数），在加压固定床连续流动反应系统上，评价其对 CO 加氢制低碳醇的催化性能，并与常规载体活性炭（AC）负载的参比物、以及不含 CNTs 的非负载共沉淀基质体系作比较。结果表明，在组成优化的 $15\%Ni_1Mo_1K_{0.05}$/CNTs 催化剂上，在 5.0 MPa，538 K，$H_2/CO/N_2$ = 45/45/10 (v/v)，GHSV(outlet)＝5000 $mL_{STP}•h^{-1}•g_{-cat}^{-1}$(outlet)的反应条件下，CO 加氢的转化率达 11.9%，相应总含氧加氢化物（$C_{1\sim3}$-醇+DME）的时空产率达 205 $mg•h^{-1}•g_{-cat}^{-1}$。这个值是相同条件下 AC 负载最佳($Ni_1Mo_1K_{0.05}$)-载量的参比催化剂（$35\%Ni_1Mo_1K_{0.05}$/AC）的相应值（176 $mg•h^{-1}•g_{-cat}^{-1}$）的 1.16 倍，是不含 CNTs 的非负载共沉淀基质体系（$Ni_1Mo_1K_{0.05}$）的相应值（116 $mg•h^{-1}•g_{-cat}^{-1}$）的 1.76 倍。

1.2 CNTs 负载 Ni-Mo-K 氧化物基催化剂的表征

催化剂的物化（XRD，XPS，H_2-TPD 和 LRS 等）表征结果揭示，CNTs-载体通过其与被担载 Ni-Mo 组分的相互作用，对催化剂的化学态产生强烈影响，导致工作态催化剂上与低碳醇的生成密切相关的两类表面催化活性物种，NiO(OH)和 Mo^{4+}/Mo^{5+}，的摩尔分率明显增加，相应地，与烃的生成（尤其 CO 加氢甲烷化）密切相关的两类表面催化活性物种，Ni^0 和 Mo^0，的摩尔分率大为下降。此外，CNTs 载体还为 H_2 的吸附活化提供 sp^2-C 表面活性位。所有这些因素都有助于 CO 加氢生成 $C_{1\sim3}$-醇的选择性的提高。

2. CO 加氢制低碳醇用 Ni 修饰 CNTs 促进的共沉淀型 Ni-Mo-K 氧化物基催化剂的开发研究

2.1 金属镍修饰 CNTs-基纳米材料的研制

以自行制备的一种鱼骨型 CNTs 作为基质，用微波助多元醇液相还原沉积法制备一类金属 Ni-修饰的 CNTs，记为 y%Ni/CNTs（y%为质量百分数）。所制得的复合材料的 TEM/SEM 观测结果显示，金属 Ni 相当均匀地高度分散在 CNTs 表面；利用 Scherrer 公式，从金属 Ni 的 XRD 特征衍射峰的半峰宽度可估算出其粒径在 6 nm 以下。组成为

4.8%Ni/CNTs 试样的 EDX 分析显示，C、O、Ni 为该试样表面层仅有的 3 种元素，其原子百分率分别为 94.4%、4.5%和 1.1%。H_2-TPD 测试揭示，适量金属 Ni 对 CNTs 表面的修饰导致其对 H_2 的吸附容量显著增加，以组成 4.8%Ni/CNTs 试样对 H_2 的吸附容量增幅最大（两试样在 293～873 K 温度范围的 H_2-TPD 曲线的相对面积强度比为 $S_{4.8\%Ni/CNTs}/S_{CNTs}$ = 100/32，增幅达 212%）。

2.2 金属 Ni 修饰 CNTs 促进的共沉淀型 Ni-Mo-K 氧化物基催化剂的制备和催化性能

用上述制备的金属 Ni 修饰的 CNTs（*y*%Ni/CNTs）作为促进剂，制备 *y*%Ni/CNTs-促进的共沉淀型 Ni-Mo-K 催化剂，记为 $Ni_iMo_jK_k$-*x*%(*y*%Ni/CNTs)（*x*%和 *y*%均为质量百分数）。在加压固定床连续流动反应系统上评价其对 CO 加氢制低碳醇的催化性能，并与添加等量纯 CNTs 的对应物和不添加 CNTs 的原基质催化剂作比较。结果表明，在组成经优化的 $Ni_1Mo_1K_{0.05}$-10.8%(4.8%Ni/CNTs)催化剂上，在 5.0 MPa、558 K、$H_2/CO/N_2$ ＝45/45/10 (v/v) 和 5000 $mL_{STP}•h^{-1}•g_{-cat}^{-1}$ (outlet) 的反应条件下，CO 加氢的转化率达 18.0%，总加氢含氧产物（$C_{1\sim3}$-醇+DME）的时空产率达 379 $mg•h^{-1}•g_{-cat}^{-1}$；这个值是添加等量纯 CNTs 的对应物 $Ni_1Mo_1K_{0.05}$-10.8%CNTs 的相应值（317 $mg•h^{-1}•g_{-cat}^{-1}$）的 1.2 倍，是不添加 CNTs 的原基质催化剂 $Ni_1Mo_1K_{0.05}$ 的相应值（218 $mg•h^{-1}•g_{-cat}^{-1}$）的 1.7 倍。在总加氢产物中，（$C_{1\sim3}$-醇+DME）的 C-基选择性达 70.3%，以 EtOH 为主要加氢产物，其 C-基选择性达 24.2%，展现其作为优质车用动力燃料添加剂和化工原料的重要应用前景。

2.3 金属 Ni 修饰 CNTs 促进的共沉淀型 Ni-Mo-K 氧化物基催化剂的表征

表观活化能的测试结果表明，添加少量 CNTs-基促进剂于共沉淀型 Ni-Mo-K 氧化物基催化剂中并不引起 CO 加氢反应的表观活化能发生明显变化，暗示少量碳纳米管基促进剂的参与并不导致 CO 加氢制低碳醇反应的速率决定步骤有所改变。催化剂的氧化态前驱物的 H_2-TPR 测试结果显示，与不添加 CNTs 基促进剂的共沉淀基质体系相比，添加 CNTs 基促进剂的体系更易于在较低温度下还原活化。工作态催化剂的 XRD 和 XPS 谱揭示，CNTs-基促进剂通过其与 Ni-Mo 组分的相互作用，对催化剂的化学态有显著影响，导致在工作态催化剂表面，与低碳醇生成密切相关的两类催化活性物种，NiO(OH)

和 Mo^{4+}/Mo^{5+}，的摩尔分率明显增加，与此同时，与烃的生成（尤其是 CO 加氢甲烷化）密切相关的两类催化活性物种，Ni^0 和 Mo^0，的摩尔分率大为下降。H_2-TPD 和 LRS 联合表征结果揭示，CNTs-基促进剂对 H_2 强的吸附能力在工作态催化剂表面营造高浓度的 sp^2-C–H 吸附物种的微环境，于是有助于提高一系列表面加氢反应的速率，并抑制水煤气变换副反应。所有这些因素对 $C_{1\sim3}$-醇产率的提高都有不同程度的贡献。

对比研究揭示，与由类石墨平面“边沿原子”构建而成的鱼骨型多壁碳纳米管管壁表面富含悬键的情形不同，平行型多壁碳纳米管的管壁表面系由类石墨平面“面内原子”构建而成，较少悬键，化学活性较低，相应工作态催化剂表面 sp^2-C–H 形态的 H-吸附物种的浓度较低，其促进作用不如鱼骨型 CNTs 显著。在相同条件下，添加等量平行型 CNTs 的催化剂上低碳醇醚产物（$C_{1\sim3}$-醇+DME）的单程时空产率只及添加以鱼骨型 CNTs 的对应体系的 67%（即：212 : 317 ($mg\bullet h^{-1}\bullet g_{\text{-cat}}^{-1}$)，在 5.0 MPa、558 K 的反应条件下）。同为碳素材料的 AC（一种比表面积高达 830 m^2/g 的无定形碳），由于其不具备 CNTs 特有的纳米级石墨化管壁结构，等量 AC 的掺入不仅无助于 $Ni_1Mo_1K_{0.05}$ 基质催化剂性能的提高，反而导致 CO 加氢转化率和低碳醇醚产率有所下降（可能由于其对 Ni-Mo 活性组分的稀释之故）。

3. 结论

1) CNTs-基纳米材料（包括纯 CNTs 和金属 Ni-修饰 CNTs）能作为合成气加氢转化制低碳醇用 Ni-Mo-K 氧化物基催化剂的优良载体或促进剂。在本文研制的 CNTs-基纳米材料负载或促进的 $Ni_1Mo_1K_{0.05}$ 氧化物基催化剂上，在经优化的反应条件下，合成气加氢转化均显示出高的生成 $C_{1\sim3}$-醇的选择性。
2) CNTs-基纳米材料的促进作用主要表现在：a) 为反应物之一的 H_2 的吸附活化提供 sp^2-C 表面活性位，在工作态催化剂表面营造高浓度 sp^2-C–H 吸附物种的微环境；b) 通过影响催化剂的化学态，促进工作态催化剂表面与低碳醇醚生成密切相关的两种催化活性物种，NiO(OH)和 Mo^{4+}/Mo^{5+}，的摩尔分率显著提高。
3) 少量金属 Ni 对 CNTs 的适当修饰能提高 CNTs 对 H_2 的吸附能力，使其促进作用更显著。

4. 本文的创新点

- 研发出一种金属 Ni 修饰 CNTs 促进的高效新型 Ni-Mo-K 氧化物基催化剂，所制备的催化剂用于合成气加氢转化，能有效地提高生成低碳醇醚（$C_{1\sim3}$-醇+DME）的选择性和单程产率，具有实用前景。
- 初步弄清作为载体或添加剂的 CNTs-基纳米材料的促进作用本质，对于深化对 CNTs-基纳米材料的催化特性的认识具有理论意义。

关键词：多壁碳纳米管；金属 Ni-修饰碳纳米管；Ni-Mo-K 催化剂；CO 加氢；低碳醇合成

Extended Abstract

The higher alcohols (C_{2+}-alcohols), together with methanol and dimethyl ether (DME), have been considered as the most important species among coal-based clean synthetic fuels and chemical feedstocks. The higher alcohols have been confirmed to be a better and cleaner automobile fuel. They feature high octane numbers, and lower emissions of NO_x, ozone, CO, and aromatic vapors. Recently, use of methyl *tert*-butyl ether (MTBE) has been prohibited in some countries or regions as additive of oil-based fuel due to the new regulations in environment protection. This change has greatly renewed interest in conversion of syngas via hydrogenation to C_{2+}-oxygenates as gasoline blends.

Higher alcohol synthesis (HAS) on the catalysts containing Mo, Group VIII metals and alkali have been extensively studied since the 1980s. Progress in this field has contributed considerably to the growing understanding of the nature of those catalytic reaction systems. Nevertheless, the existing technology of HAS is still on a small scale. The single-pass-conversion of the feed syngas and selectivity to C_{2+}-alcohols are both relatively low. Most systems produce methanol (over alkali-promoted MoS_2 catalysts) or hydrocarbons (over modified Fischer-Tropsch catalysts) as the main product instead of C_{2+}-alcohols. Development of catalysts with high efficiency and selectivity for HAS has been one of the key objectives for R&D efforts.

Multiwalled carbon-nanotubes (symbolized as “MWCNTs” and simplified as “CNTs”), as a type of novel nano-carbon support or promoter of catalyst, have been drawing increasing attention since their discovery. This kind of nanotube-C possesses several unique features, such as highly graphitized tube-wall, nanosized channel and sp^2-C-constructed surface. They also display exceptionally high mechanical strength, high thermal/electrical conductivity, medium to high specific surface areas, and excellent performance for adsorption and spillover of hydrogen, which render this kind of nanostructured carbon materials full of promise as a novel support or promoter of catalyst. The catalytic studies conducted so far on CNT-based systems have shown encouraging results in terms of activity and selectivity.

In the present wrok, a series of Ni-Mo-K oxide-based catalysts supported or promoted by the simple CNTs or metallic Ni-decorated CNTs were developed. The performance of the catalyst for HAS from syngas was evaluated, and compared with the related reference

systems. The catalysts were characterized by means of SEM/TEM/EDS, XRD, XPS, LRS and H_2-TPD, and the nature of promoter action by the CNT-based nano-materials was discussed. The results shed some light on understanding the mechanism of promoter action by the CNT-additive and on the design of practical catalysts for the HAS. The progress obtained in the present work was briefly described as follows.

1. Development of CNTs-supported Ni-Mo-K catalysts for HAS from syngas

1.1 Performance of CNTs-supported Ni-Mo-K oxide-based catalyst for HAS from syngas

With a kind of home-made "Herringbone-type" multi-walled carbon nanotubes (noted as "CNTs") as support, a type of novel CNT-supported Ni-Mo-K catalysts for HAS from syngas were prepared by a stepwise incipient wetness method, and their catalytic activity for HAS from syngas was evaluated and compared with that of the counterpart supported on activated carbon (AC) and non-supported co-precipitated Ni-Mo-K reference system. The results showed that over the 15%$Ni_1Mo_1K_{0.05}$/CNTs catalyst under the reaction conditions of 5.0 MPa, 538 K, $H_2/CO/N_2$ = 45/45/10 (v/v) and GHSV = 5000 $mL_{STP}•h^{-1}•g_{\text{-cat}}^{-1}$ (outlet), the observed C-based selectivity of the oxygenate products ($C_{1\sim3}$-alc.+DME) reached 59.0% at the CO hydrogenation-conversion of 11.9%, with the corresponding space-time-yield (STY) of total oxygenate products reaching 205 $mg•h^{-1}•g^{-1}$. This value was 1.16 times that (176 $mg•h^{-1}•g_{\text{-cat}}^{-1}$) of the 35%$Ni_1Mo_1K_{0.05}$/AC catalyst with the optimal $Ni_1Mo_1K_{0.05}$ loading, and 1.76 times that (116 $mg•h^{-1}•g_{\text{-cat}}^{-1}$) of the CNT-free non-supported co-precipitated $Ni_1Mo_1K_{0.05}$ host system, under the same reaction conditions.

1.2 Characterizations of CNTs-supported Ni-Mo-K oxide-based catalyst

The results of the catalyst characterizations by XRD and XPS revealed that the CNT-support has strong influence on the chemical states of catalyst via its interaction with the supported Ni-Mo components, leading to the increase of the molar percentage of NiO(OH) and Mo^{4+}/Mo^{5+} (the two kinds of catalytically active surface-species associated closely to selective formation of $C_{1\text{-}3}$-alcohols) and the dramatic decrease of the molar percentage of Ni^0 and Mo^0 (the two kinds of catalytically active surface-species associated closely to selective formation of hydrocarbons, especially methanation of CO). On the other hand, the

CNT-support also provided the sp^2-C surface-sites for adsorption-activation of H_2, which would generate surface micro-environments with high stationary-state concentration of H-adspecies in the form of sp^2-C–H on the functioning catalyst. Those active H-adspecies could be readily transferred to $Ni_iMo_jK_k$ active sites via CNT-promoted hydrogen-spillover and thus increase the rate of surface hydrogenation reactions in the HAS. The aforementioned factors all contribute to an increase in selectivity of generating $C_{1\sim3}$-alcohols.

2. Development of metallic Ni-decorated CNTs-promoted co-precipitated Ni-Mo-K oxide-based catalyst for HAS from syngas

2.1 Preparation and characterization of metallic Ni-decorated CNTs

With the home-made "Herringbone-type" CNTs as substrate, a type of metallic Ni-decorated CNTs (symbolized as *y*%Ni/CNTs, where *y*% represents mass percentage) was prepared via a microwave irradiation-assisted polyol-reduction/deposition method, with 4.8% of Ni-loading amount being the optimal, as evidenced by the optimization tests. The results of characterization by TEM/SEM/EDX and XRD showed that, in the prepared 4.8%Ni/CNTs, the metallic Ni nanoparticles were fairly uniform in shape and size and well dispersed on the surface of CNTs, with the Ni-particle diameters being below 6 nm, and C, O and Ni were the only three elements at the surface of 4.8%Ni/CNTs, with atomic percentage of 94.4%, 4.5% and 1.1%, respectively. The H_2-TPD test revealed that the modification of an appropriate amount of metallic Ni to the CNTs led to a significant increase in their hydrogen-adsorbing capacity, with the 4.8%Ni/CNTs reaching a maximum increment of 2.1 times (with the ratio of relative area-intensity of the observed H_2-TPD profiles estimated to be $S_{4.8\%Ni/CNTs}/S_{CNTs}$ = 100/32) in the temperature range of 273~873 K.

2.2 Performance of metallic Ni-decorated CNT-promoted co-precipitated Ni-Mo-K oxide-based catalyst for HAS from syngas

Using the *y*%Ni/CNTs as promoter, a type of co-precipitated Ni-Mo-K oxide-based catalysts, noted as $Ni_iMo_jK_k$-*x*%(*y*%Ni/CNTs), was developed, with excellent performance for the selective formation of $C_{1\sim3}$-alcohols from syngas. Over the composition-optimized

catalyst of $Ni_1Mo_1K_{0.05}$-10.8%(4.8%Ni/CNTs) under reaction condition of 5.0 MPa, 558 K, $H_2/CO/N_2$ = 45/45/10 (v/v) and GHSV = 5000 $mL_{STP}•h^{-1}•g_{-cat}^{-1}$ (outlet), the observed conversion of CO hydrogenation reached 18.0%, with the corresponding STY of total oxygenate products ($C_{1\sim3}$-alc.+DME) being 379 $mg•h^{-1}•g_{-cat}^{-1}$. This value of $STY_{Total\text{-}oxy.}$ was 1.2 and 1.7 times that (317 $mg•h^{-1}•g_{-cat}^{-1}$) of the simple CNT-doped counterpart ($Ni_1Mo_1K_{0.05}$-10.8%CNTs) and that (218 $mg•h^{-1}•g_{-cat}^{-1}$) of CNT-free host system, $Ni_1Mo_1K_{0.05}$, respectively, under the same reaction condition.

2.3 Characterization of metallic Ni-decorated CNT-promoted co-precipitated Ni-Mo-K oxide-based catalyst

The addition of a minor amount of the Ni-decorated CNTs into the $Ni_iMo_jK_k$ host catalyst caused little change in the apparent activation energy for the HAS, but led to the increase of the molar percentage of NiO(OH) and Mo^{4+}/Mo^{5+} (the two kinds of catalytically active surface-species associated closely to selective formation of $C_{1\text{-}3}$-alcohols) and the dramatic decrease of the molar percentage of Ni^0 and Mo^0 (the two kinds of catalytically active surface-species associated closely to selective formation of hydrocarbons, especially methanation of CO), as evidenced by our XPS and XRD investigations of the tested catalysts.

The laser Raman spectroscopic (LRS) studies revealed that the difference of the CNT-containing co-precipitated catalysts, $Ni_1Mo_1K_{0.05}$-10.8%(4.8%Ni/CNTs) and $Ni_1Mo_1K_{0.05}$-10.8%CNTs, from the CNT-free $Ni_1Mo_1K_{0.05}$ host system lies not simply in their capability of adsorbing hydrogen, but also in the property of H-adspecies on the two types of systems. The H-adspecies detected on the H_2-prereduced catalysts of $Ni_1Mo_1K_{0.05}$-10.8%(4.8%Ni/CNTs) and $Ni_1Mo_1K_{0.05}$-10.8%CNTs were the H(a) adsorbed on sp^2-C-sites (with the ν_{C-H} at 2935 and 3233 cm^{-1} for -CH_2 and -CH, respectively), while those detected on the H_2-prereduced $Ni_1Mo_1K_{0.05}$ host were the H(a) adsorbed on Ni^0-sites and Mo^0-sites (with the ν_{Ni-H} and ν_{Mo-H} at 1983 and 1878 cm^{-1}, respectively). On the CNT-free $Ni_1Mo_1K_{0.05}$ host system, high hydrogenation activity of H-species adsorbed zero-valence metal (Ni^0 and Mo^0) sites enhanced the tendency of CO hydrogenation to generate hydrocarbon, thus leading to considerable increase of $S_{Total\text{-}HC}$, together with marked decrease of $S_{Total\text{-}oxy.}$.

It could be inferred from the H_2-TPD measurements that the excellent adsorption performance of the CNTs, especially Ni-decorated CNTs, for H_2 would be conducive to

generating a surface micro-environment with a high stationary-state concentration of H-adspecies in the form of sp^2-C–H on the functioning catalyst. Those active H-adspecies could be readily transferred to the $Ni_iMo_jK_k$ sites active catalytically via the CNT-promoted hydrogen-spillover, thus increase the rate of a series of surface hydrogenation reactions. In addition, high concentration of H-adspecies on the catalyst would also greatly inhibit the water-gas-shift side-reaction. All these factors mentioned above contribute to an increase in the yield of $C_{1\sim3}$-alcohols.

Compared to that of the "Herringbone-type" CNTs, the surface of the "Parallel-type" CNTs possesses less dangling bonds, thus lower chemical activity. It is probably this peculiarity that renders the "Parallel-type" CNTs to have lower capability for adsorption and activation of H_2, as evidenced by H_2-TPD measurements, thus showing the rather limited promoter effect.

In sharp contrast to the CNTs(or 4.8%Ni/CNTs)-doped systems, the addition of activated carbon (AC, a kind of amorphous carbon with 830 m^2/g of N_2-BET-SSA) into the $Ni_1Mo_1K_{0.05}$ host catalyst not only did not help improve the performance of the catalyst, but also led to a certain decrease in conversion of the CO hydrogenation and STY of the total oxygenate products ($C_{1\sim3}$-alc.+DME).

3. Conclusion

1) It is evident that the CNTs or CNT-based materials decorated by metallic Ni could act as a novel carrier and/or promoter of the Ni-Mo-K oxide-based catalyst for HAS from syngas. The (4.8%Ni/CNTs)-doped co-precipitated $Ni_1Mo_1K_{0.05}$ catalyst achieves highly effective and selective formation of $C_{1\sim3}$-alcohols from syngas.
2) The promoter action by the CNTs was mainly in providing the sp^2-C surface-sites for adsorption-activation of H_2 (one of the reactants), while simultaneously enhancing the molar percentage of the two kinds of surface species active catalytically, NiO(OH) and Mo^{4+}/Mo^{5+} (both associated closely to selective formation of $C_{1\text{-}3}$-alc.), via affecting the chemical states of catalyst.
3) Appropriate decoration of the CNTs by a minor amount of metallic Ni could improve the capability of CNT's adsorbing H_2, rendering their promoter action more remarkable.

The results of the present work also shed some light on the understanding of the promoter

action by the transition metal-decorated CNTs-additive and on the design of practical catalyst for HAS from syngas. For better understanding of nature of the promoting action by CNT-based nano-materials, especially the mechanism of improving selective formation of the higher (C_{2+}) alcohols, further studies, especially *in-situ* characterization of reaction intermediates under the HAS reaction condition, are highly needed.

Keywords: Multi-walled carbon nanotubes; metallic Ni-decorated MWCNTs; Ni-Mo-K catalyst; CO hydrogenation; higher alcohol synthesis

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